

tilities of disilyl ether and disilane are similar (b.p. -15.2 and -14.5° , respectively), whereas digermyl ether with a maximum vapor pressure of 66 mm. at 0° is appreciably less volatile than digermane (v.p. of 243 mm. at 0°) thus suggesting a considerably larger dipole moment for $(\text{GeH}_3)_2\text{O}$. In view of the near equality of the electronegativities of germanium and silicon, this result is in agreement with a highly bent Ge-O-Ge skeleton.

If the near linearity of the Si-O-Si linkage in disilyl ether is correctly explained¹⁰ as a result of a ($p \rightarrow d$) π -bonding contribution, then this contribution to the bonding in digermyl ether would be negligible if it has a highly bent skeleton as indicated by the above result. The difference in bonding between germanium and silicon may appear surprising since the covalent radii, electronegativities, and ionization potentials of the

two elements are almost identical. None of these properties, however, reflects the difference in spatial distributions of the 3d- and 4d-orbitals and their relative abilities to form π -type bonds with oxygen 2p-orbitals. Indeed, bonding properties reflect relatively small perturbations on electron distributions and the very low bending frequency of disilyl ether⁶ resulting from a low angle-bending force constant suggests that a small change in orbital overlap or repulsion terms could appreciably change the equilibrium angle.

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Rare Gas Ion Reactions with Ammonia¹

BY G. R. HERTEL AND W. S. KOSKI

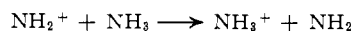
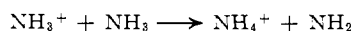
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The fractional yields and the relative cross sections for rare gas ion reactions with ammonia have been determined for the 3 to 200 e.v. energy region. The results are in rough agreement with the Massey-Burhop theory; however, anomalies are present. The implication of these results is discussed with respect to the recently proposed mechanism for rare gas sensitization for the production of hydrazine in the gas phase radiolysis of ammonia.

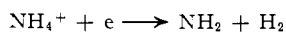
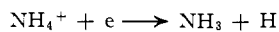
Introduction

Recently Lampe, *et al.*,² had occasion to investigate hydrazine formation in the gas phase radiolysis of ammonia. Deuterons were used as a source of ionizing radiation and the influence of the addition of Kr and Ne on the yield of hydrazine was investigated.

The yield of hydrazine increased by a factor of about 20 when the irradiated gas composition was changed from 90 mole % Ne in a Ne-NH₃ mixture to 90 mole % Kr in a Kr-NH₃ mixture. The proposed mechanism in the pure NH₃ case consisted of the ionization of NH₃ to produce NH₃⁺ and NH₂⁺ which was followed by the reactions

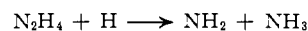
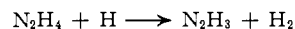


The neutralization of NH₄⁺ was considered to be the only important neutralization process. The reactions proposed were



Hydrazine formation was pictured as resulting from the recombination of two amino radicals. On the basis of the work of McDonald, Kahn, and Gunning,³

it was concluded that hydrazine is efficiently destroyed by hydrogen atoms in the reactions



Therefore in this proposed mechanism the primary reason for the low *G*-value for hydrazine production is the destruction of hydrazine by hydrogen atoms.

In the presence of Kr or Ne, rare gas ions are produced by the deuteron bombardment, and charge exchange occurs between the rare gas ion and NH₃. The semiquantitative theory of Massey and Burhop⁴ may be expected to be applicable. In this theory the maximum cross section for charge exchange is expected to occur for the condition

$$v_m = a |\Delta E| / h$$

and for $v \ll v_m$ the expression for the cross section will be of the form

$$\sigma \sim e^{-a|\Delta E|/4hv}$$

where v = relative ion velocity, v_m = relative ion velocity at maximum cross section, $a = \sim 7 \times 10^{-8}$ cm., ΔE is the energy defect and is the difference between the recombination energy of the bombarding ion and the energy required to produce the particular state of the product ion.

In the presence of Xe⁺, the ion NH₃⁺ would be expected to be produced in largest yield, whereas other

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract AF 49(638)-481.

(2) F. W. Lampe, W. S. Koski, E. R. Weiner, and W. H. Johnston, *Intern. J. Appl. Radiation Isotopes*, **14**, 231 (1963).

(3) C. C. McDonald, A. Kahn, and H. E. Gunning, *J. Chem. Phys.*, **22**, 908 (1954).

(4) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, p. 478.

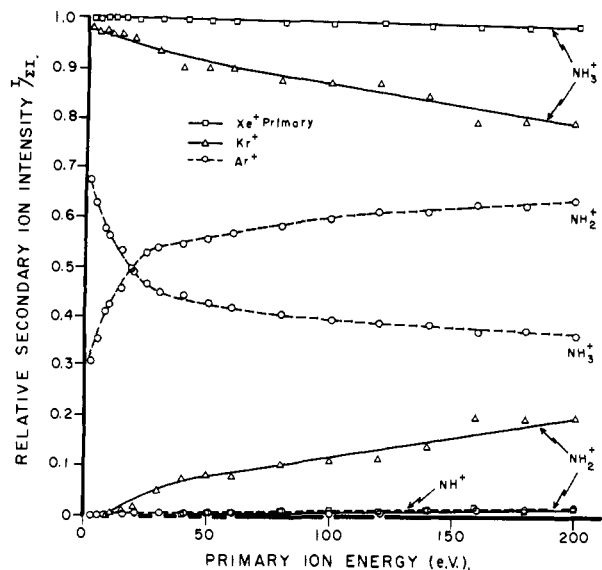


Fig. 1.—Fractional ion yields of secondary ions *vs.* rare gas ion energy for the reactions $\text{NH}_3 + (\text{Xe}^+, \text{Kr}^+, \text{and } \text{Ar}^+) \rightarrow$ products.

ions such as NH_2^+ , NH^+ , etc., would be produced with small yields rising with bombarding energy. In the case of Ne^+ , because of the much higher ionization potential of neon, the reaction



would be expected to be more probable than the corresponding one to produce NH_3^+ . Since it has been demonstrated that H atoms lead to destruction of hydrazine, one would expect to have larger yields of N_2H_4 when Xe or Kr is used to sensitize the reaction than if Ne is used for the purpose.

The study of the reaction of rare gas ions with NH_3 was therefore undertaken with the objective of getting a better understanding of the mechanism of formation of N_2H_4 in the radiolysis of ammonia.

Experimental

The apparatus used in this work has been described elsewhere.⁵ It consists of a pair of mass spectrometers in tandem. The primary ion beam is generated by a 180° magnetic spectrometer having a 1-cm. radius of curvature. The ion beam from this primary mass spectrometer (PMS) passes between deflection plates and enters an ion lens which focuses it into a reaction chamber. This lens also adjusts the ion acceleration to any value between 2 and 200 v.

The primary ion beam crosses the reaction chamber at right angles to the direction in which the secondary ions are extracted through the exit slit. After extraction from the reaction chamber, the secondary ions are accelerated to 2 or 3 kev. and mass analyzed in an 8-in. radius, 60° magnetic sector mass spectrometer. A 14-stage DuMont Type SP-172 electron multiplier was used as a detector, and individual ions were counted using suitable counting equipment.

The rare gases used in this work are of research grade and were purchased from the Matheson Co. The target gas was anhydrous ammonia obtained from the same company.

The general procedure was to adjust the ammonia pressure to the same value for each rare gas ion and then the secondary ion yield was measured for various values of the beam energy. Each point on the graph represents the average of several measurements. Manifold pressures were monitored with a Consolidated Type GIC-011 ionization gage.

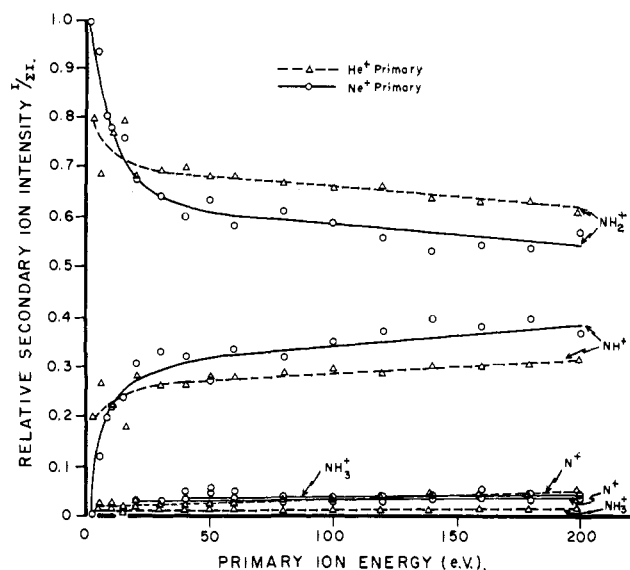


Fig. 2.—Fractional ion yields of secondary ions *vs.* rare gas ion energy for the reactions $\text{NH}_3 + (\text{He}^+, \text{Ne}^+) \rightarrow$ products.

Results and Discussion

Figures 1 and 2 give the results plotted as fractional ion yield of secondary ions *vs.* the rare gas ion energy. In the case of Xe^+ bombardment, the only secondary ion produced in significant amounts was NH_3^+ . The NH_2^+ ion was present in very small amounts which increased slowly with bombarding energy. The abundances of other nitrogen-containing ions in this case were negligible. When one proceeds to the case of Kr^+ , the energy defect, ΔE , becomes larger for the production of NH_3^+ but smaller for the production of NH_2^+ . Consequently, the relative amount of NH_2^+ is greater in the Kr^+ case than in the Xe^+ case.

In the Ar^+ case, the condition for production of NH_2^+ is almost resonant, assuming ground states are involved, so this ion would be expected to be present in largest abundance followed by NH_3^+ and NH^+ . Also, the resonance condition would predict a high abundance of NH_2^+ at low energies with decreasing abundance as the argon energy increased. This is precisely the opposite of what is observed. However, the possible role of excited states of these ionic fragments must not be overlooked. McDowell⁶ reports the first excited state of the NH_3^+ ion as 15.31 e.v. Thus, the probability of producing excited NH_3^+ ions should be relatively high and this reaction may compete favorably with the reaction in which NH_2^+ ions are formed. Indeed, when one surveys the literature, one notes variations as high as several tenths of an electron volt in the reported values of appearance potentials of various ions and their excited states, so that it appears entirely possible that the formation of excited NH_3^+ in the Ar^+-NH_3 reaction may be a more nearly resonant case than the formation of NH_2^+ ions.

In the reaction of Ne^+ with NH_3 , NH_2^+ is the most abundant ionic product followed by NH^+ , NH_3^+ , and N^+ . In this case, one might have expected NH^+ to be the most abundant ion present in the products. The He^+-NH_3 reaction also yields NH_2^+ as the most abundant ion followed by NH^+ , N^+ , and NH_3^+ . On the basis of the Massey-Burhop picture, one would

(5) E. R. Weiner, G. R. Hertel, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 788 (1964).

(6) C. A. McDowell, *J. Chem. Phys.*, **24**, 618 (1956).

have predicted high yields of both N^+ and NH^+ with relatively small amounts of NH_2^+ and NH_3^+ .

Again, one is led to consider the possibility of excited states to account for the observed results. Estimates of the energies needed to produce various excited states of NH_2^+ from NH_3 , based on calculations made by Ellison,⁷ indicate that this explanation is at least reasonable.

It therefore appears that the Massey-Burhop theory can be crudely applied to the rare gas ion-ammonia reaction; however, the various possibilities, afforded by the presence of numerous excited states in the molecular-ion products, make prediction of the results complicated and uncertain.

The relative cross sections for the various reactions in question have also been measured and they are illustrated graphically in Fig. 3. Again some of the results are consistent with the adiabatic picture. The reactions with Xe^+ , Kr^+ , and Ar^+ fall into this category. On the other hand, the relative cross sections obtained for reactions with Ne^+ are anomalously low. The reason for this is not yet certain and is being studied further. One explanation that suggests itself is that collisional excitation of the molecule occurs when the masses of the colliding ion and molecule are approximately the same. When such conditions prevail, one might expect the energy defect to be significantly larger than in the corresponding situation where the ground states would be involved and hence the cross section for the reaction in question would be lower.

We may now examine the significance of these results as far as the mechanism of the hydrazine formation in the gas phase radiolysis of ammonia is concerned. It should be noted in this discussion that the rare gas ion energies in this study do not correspond to those expected under the radiolysis conditions. However, it appears that some relevant conclusions can be drawn. It is clear that the results obtained with Xe^+ , Kr^+ , and Ar^+ are not incompatible with the proposed mechanism since one would expect progressively larger amounts of hydrogen atoms as one proceeds from the high to low mass ions and the presence of increasing amounts of H would lead to greater destruction of hydrazine with a corresponding lowering of the yield. On the other hand, the low cross sections for the neon reactions throw considerable doubt on the validity of the mechanism. While it is true NH_2^+ and thus H atoms are the most abundant species produced in the Ne^+ reactions, the yields of all ionic products are very low compared to the other rare gas ion-ammonia reactions. Thus, a very reasonable and direct explanation for the low G -value is simply a lack of amino radicals

(7) F. O. Ellison, *J. Chem. Phys.*, **36**, 3107 (1962).

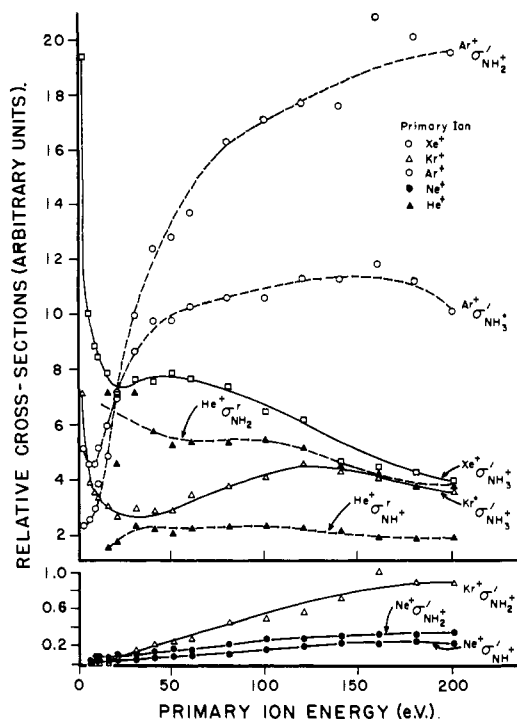


Fig. 3.—Relative cross sections vs. bombarding ion energy for various rare gas ions reacting with ammonia.

due to the small probability of reaction between Ne^+ and NH_3 . These results further suggest that it would be instructive to study the ammonia radiolysis using the other rare gases as sensitizers. For example, $Ar^+ + NH_3$ has a very high relative cross section for $NH_2^+ + H$ production; consequently, if H atom destruction is the explanation for the low hydrazine yield, the G -value for hydrazine production when argon is used as a sensitizer should be at a minimum. These conclusions must be of a tentative nature since our equipment did not permit us to study these ion molecule reactions above 200 e.v. energy, and it is not unlikely that the $Ne^+ + NH_3$ reaction cross section will rise significantly at much higher bombarding energies.

Finally, it may be stated that we have also observed the NH_4^+ ion in the products and this very probably arises from the $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ reaction. In addition in the argon ion reactions, we have observed a small mass peak corresponding to $(ArNH)^+$. However, the corresponding ion was not observed with the other rare gases.

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